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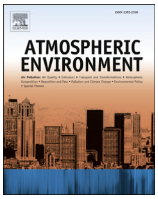

Global modeling study of soluble organic nitrogen from open biomass burning

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HIGHLIGHTS

- Soluble ON deposition is simulated with and without open biomass burning.
- Differences between two simulations include both emission and secondary formation.
- Enhanced soluble ON concentration is found in two simulations during fire events.
- Multiphase chemical source of soluble ON is examined in a global model.
- Atmospheric processing may have a significant effect on the deposition of soluble ON.

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ABSTRACT

Atmospheric deposition of reactive nitrogen (N) species from large fires may contribute to enrichment of nutrients in aquatic ecosystems. Here we use an atmospheric chemistry transport model to investigate the supply of soluble organic nitrogen (ON) from open biomass burning to the ocean. The model results show that the annual deposition rate of soluble ON to the oceans (14 Tg N yr^{-1}) is increased globally by 13% with the increase being particularly notable over the tropical oceans downwind from the source regions. The estimated deposition of soluble ON due to biomass burning from the secondary formation (1.0 Tg N yr^{-1}) is close to that from the primary sources (1.2 Tg N yr^{-1}). We examine the secondary formation of particulate C—N compounds (i.e., imidazole, methyl imidazole, and N-containing oligomers) from the reactions of glyoxal (CHOCHO) and methylglyoxal (CH_3COCHO) with ammonium (NH_4^+) in wet aerosols and upon cloud evaporation. These ON sources result in a significant contribution to the open ocean (1.3 Tg N yr^{-1}), suggesting that atmospheric processing in aqueous-phase may have a large effect. We compare the soluble ON concentration in aerosols with and without open biomass burning as a case study in Singapore. The model results demonstrate that the soluble ON concentration in aerosols is episodically enriched during the fire events, compared to the case without smoke simulations. At the same time, the model results show that the daily soluble ON concentration can be also enhanced in the case without smoke simulations, compared to the monthly averages. These results may suggest that both the primary source strength of ON and the secondary formation rates of ON should be taken into consideration when using *in-situ* observations to constrain the calculated soluble ON burden due to biomass burning. More accurate quantification of the soluble ON burdens both with and without smoke sources is therefore needed to assess the effect of biomass burning on bioavailable ON input to the oceans.

1. Introduction

Organic component of atmospheric nitrogen (N) may play an important role in biogeochemical cycles, climate, and ecosystems (Duce et al., 2008; Cornell, 2011). Atmospheric organic nitrogen (ON) is associated with anthropogenic activities, biomass burning, mineral dust, and marine biological sources (Jickells et al., 2013). Analysis of specific ON components in the aqueous-phase (rain or cloud) leads to the identification of oxidized ON compounds (e.g., organic nitrates and nitrophenols) and reduced ON compounds (e.g., amines, amino acids and urea) (Cape et al., 2011). The oxidized

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ON in the atmosphere can be produced by the reactions of volatile organic compounds (VOCs) with nitrogen oxides (NO_x) through a variety of reaction pathways (e.g., Neff et al., 2002: Ito et al., 2007a; Goldstein et al., 2009). Reduced ON compounds (e.g., imidazole, imidazole-2-carboxaldehyde, and biimidazole) have been identified as a product of reactions of glyoxal and methylglyoxal with ammonium sulfate ($(NH_4)_2SO_4$), amino acids, and amines in laboratory studies (De Haan et al., 2009a, 2009b, 2011; Galloway et al., 2009; Yu et al., 2011; Kampf et al., 2012). Organic N-containing compounds can also be directly emitted during vegetation fires, because substituted N-heterocyclic compounds typically undergo minor pyrolytic and oxidative fragmentations at relatively low temperatures (i.e., smoldering fires) (Mukai and Ambe, 1986; Laskin et al., 2009).

Laboratory experiments conducted with ammonium salts indicate that imidazoles corresponded to only a very small fraction (<1%) of total observed organic aerosol in a study of glyoxal uptake on ammonium sulfate seed aerosol (Galloway et al., 2009). A regional modeling study showed that the ammonium pathway contributed a very small fraction of predicted SOA mass concentration over California (Knote et al., 2014). Although it appears unlikely that the reaction of glyoxal with ammonium contributes significantly to ambient SOA mass in acidic or non-marine aerosols, the reactions of glyoxal and methylglyoxal with ammonium may still be a significant atmospheric source of brown carbon, imidazoles, and N-containing oligomers in marine aerosols (Sedehi et al., 2013). Further, these reactions are accelerated due to water evaporation and thus may be a significant source of the N-containing oligomers observed in urban and biomass burning aerosols (De Haan et al., 2009b, 2009c, 2011; Lee et al., 2013).

Global estimates of soluble ON deposition are highly uncertain, due to uncertainties in sources, transformation, and deposition (Table 1). In global modeling studies, atmospheric deposition of total soluble ON is conventionally considered to be mainly from secondary oxidized ON (e.g., Neff et al., 2002: Ito et al., 2007a). Based on a compilation of measurements, Duce et al. (2008) suggest that atmospheric soluble ON is more abundant than that estimated in modeling studies, constituting about 30% of total reactive N deposition (i.e., oxidized and reduced inorganic and water-soluble organic forms). Based on N:C molar ratios observed for organic aerosols, Kanakidou et al. (2012) estimated that a significant amount of the primary ON emissions was from anthropogenic activities such as biomass burning, biofuel and fossil fuel combustion sources (12 Tg N yr^{-1}) while total ON emission was 27 Tg N yr^{-1}. Our atmospheric chemistry transport model showed that anthropogenic emissions (excluding all open biomass burning sources) resulted in an increase in soluble ON deposition to the oceans (total +3.5 Tg N yr^{-1}) over the twentieth century, which was accentuated over the North Pacific Ocean downwind from East Asia (Ito et al., 2014). These results highlight the necessity of improving the process-based quantitative understanding of the chemical formation of soluble ON species in the atmosphere.

Here we examine the relative contribution of soluble ON from open biomass burning to the total deposition in our atmospheric chemistry transport model. The quantification of soluble ON by minimizing the difference between modeled and observed soluble ON may be described as a ‘top-down’ approach. The alternative ‘bottom-up’ approach to the quantification of soluble ON is to identify the individual formation processes from laboratory experiments, and estimate them separately. In our previous study, we used the model to explore methods for improving the apparent underestimate in modeled ON by fitting the amount of reduced ON sources in the water absorbed by hygroscopic particles (aerosol water) to the observations of soluble ON deposition at coastal and marine locations (i.e., a top-down approach) (Ito et al., 2014). Here we use an updated version of the chemical transport model that couples the gas-phase chemistry with detailed aqueous-phase chemistry (Lin et al., 2014). We examine the source of soluble ON produced as a result of reaction of glyoxal and methylglyoxal with ammonium ions in aerosol water and during cloud evaporation, which is based on laboratory experiments (i.e., a bottom-up approach). Because of the large uncertainty in the magnitude of the contribution of this pathway to total organic aerosol mass, the purpose of the global model simulations in this study is not to predict the magnitude of soluble ON concentration measured in a specific case study but to explore relative contributions from different sources. Section 2 describes the modeling methods and the numerical experiments that were performed. The spatial distribution of soluble ON deposition and the temporal variation of soluble ON concentration with different origins are used to explore different possible explanations for enhancements in the soluble ON concentrations and deposition during fire events in Section 3. Section 4 presents a summary of the findings and the future outlook.

Table 1
Soluble organic nitrogen deposition (TgN yr^{-1}).

Study	Global deposition
Neff et al. (2002)	10
Duce et al. (2008)	(20)[a]
Kanakidou et al. (2012)	32 (16)[a]
Ito et al. (2014)	26 (10)[a]
This work[b]	19–30 (9–14)[a]

[a] Parentheses represent the depositions to the oceans only.
[b] The range represents the bottom-up and top-down estimates.

2. Model approach

2.1. Model description

The global chemical transport model used in this study is a coupled gas-phase and aqueous-phase chemistry version of the Integrated Massively Parallel Atmospheric Chemical Transport (IMPACT) model (Rotman et al., 2004; Liu et al., 2005; Feng and Penner, 2007; Ito et al., 2007a, 2014; Ito and Feng, 2010; Lin et al., 2012, 2014; Xu and Penner, 2012; Ito and Xu, 2014). The model simulates the emissions, chemistry, transport, and deposition of major aerosol species, including organic nitrogen (ON), nitrate, ammonium, particulate organic matter (POM), black carbon (BC), sulfate, mineral dust and sea spray aerosols, and their precursor gases. The model includes the microphysics of sulfate aerosol (Herzog et al., 2004; Liu et al., 2005) and the thermodynamics of ammonium, nitrate, and mineral aerosols (Jacobson, 1999; Feng and Penner, 2007; Ito and Feng, 2010; Xu and Penner, 2012; Ito and Xu, 2014) coupled to an integrated numerical solution for gas-phase and aqueous-phase photochemistry of organic compounds (Sillman, 1991; Ito et al., 2007a, 2014; Sillman et al., 2007; Lin et al., 2012, 2014) together with atmospheric transport (Rotman et al., 2004). The model is driven by assimilated meteorological fields from the Goddard Earth Observation System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO). Simulations have been performed with a horizontal resolution of 2.0° × 2.5° and 59 vertical layers with a top boundary at 0.01 hPa using the GEOS-5 assimilated meteorological fields for the year 2006.

2.2. Emission

We run the model with and without emissions of gases and aerosols from open biomass burning (Fig. 1 and Table 2). The